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- (71) Applicants
 Polymer Technology Corporation,
 30 Tripp Street,
 Framingham,
 Massachusetts 01701,
 United States of America.
- 72) Inventors
 Edward Joseph Ellis
 Joseph Charles Salamone
- (74) Agents
 Venner, Shipley & Co.

(54) Hydrophilic contact lens coating

contact lens comprising an optically clear, transparent body having a lens surface, said lens surface defining a polymeric material carrying an ionic charge, a thin layer of a polyelectrolyte complex coating said lens surface and electrostatically bound thereto, said coating comprising an ionic polymer and said polymer forming a hydrogel at the surface which absorbs water, has good water retention and is compatible with the physiological structure of the

The present invention also provides a solution and a method of treating contact lenses with the ionic polymer.

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SPECIFICATION

Hydrophilic contact lens coating

5. The present invention is concerned with contact lenses, solutions for treating contact lens surfaces and a method of Coating Contact Lenses.

it has long been known in the art that a contact lens must have surfaces that have a certain degree of hydropnilicity in order to be wet by tears thus providing unblurred vision.

Soft, hydrophilic contact lens, in addition to being wettable, provide comfort to the wearer but lack the 10 ability to correct visual deficiencies such as astigmatism since they tend to confirm to the shape of the corneai surface.

Often hydrophilic monomers can be added to a mixture of comonomers in the formation of contact lenses so that upon polymerization optically clear contact lenses result which have a certain degree of hydropnilicity. As the hydrophilic monomer content increases where it is added directly to the lens 15 composition, the physical characteristics of the lenses are affected by the increased hydration propensity of the polymeric composition.

In some cases it has been known to treat a formed contact lens with a polymerizable hydrophilic monomer to form a surface coating of hydrophilic polymer grafted to an otherwise hydrophobic polymer surface. Although effective, this method of increasing the hydrophilic character of the lens surface can suffer from 20 involved and difficult manufacturing procedures.

Present rigid and soft contact lenses sometimes retain water on their surfaces through secondary chemical bonding and as a consequence only a very thin layer of water molecules is present between the eye and the contact lens.

Soft lenses are inherently comfortable but oftentimes, as with hard lenses suffer from brief surface 25 dryness between eye blinks. State of the art technology teaches that a water soluble neutral polymer may be 25 applied to the surfaces of a hard contact lens to provide a "cushion" layer between the lens and the eye which is equated with increased wettability as well as wearer comfort and tolerance.

Dissipation of the "cushion" layer occurs rapidly in most prior art constructions, since there is little specific interaction between the mobile polymer in this layer and the lens surface. As a result the wearer begins to 30 feel discomfort and must recoat the lens surfaces.

It is an object of this invention to provide a hard or soft synthetic polymer contact lens whose surface carries a thin layer of polyelectrolyte complex coating the lens surface and electrostatically bound thereto.

It is another object of this invention to provide a method of rendering a contact lens that has an ionic surface more compatible with the eye by immersing the iens in a solution of an oppositely charged ionic 35 polymer to form a thin polyelectrolyte complex on the lens surface, which complex increases its hydrophilic character for a greater period of time relative to an untreated surface and which reduces the tendency for mucoproteins, a normal constituent of lacrimal tears, to adhere to a lens surface.

The layer or coating comprises a polyelectrolyte complex which is formed by reaction of an ionic lens surface with an oppositely charged ionic polymer, and this complex forms a hydrogel at the lens surface 40 which absorbs water, has good water retention, and is compatible with the physiological structures of the eye. A durable "cushion" is formed which provides long lasting comfort to the eye.

In the preferred embodiment, the lens is an oxygen permeable hard lens which carries an ionic charge or has the potential of having an ionic charge. Preferably the lens coating is formed by merely immersing the lens in a solution which consists essentially of an ionic polymer dissolved in a water solution or a water 45 solution containing soluble organic components comprising from 0.001 to 10% by weight of the solution. The ionic polymer can be any ionic polymer compatible with the eye and which does not cause eye irritation yet which forms a hydrogel and which is electrostatically bound to the surface of the contact lens.

It is a feature of this invention that thin coatings of from 20 to 2,500 Angstroms are formed, which coatings not only increase the compatibility of contact lens with the eye but also add a cushioning effect between the 50 lens and the eye. Such coatings can avoid problems of punctate staining and further enhance the ability of the contact lens to be worn in the eye for periods up to 24 hours or more.

Depending on the concentration of ionic sites on the lens surface and the concentration of oppositely charged ionic polymer with which the surface is reacted, either wetting, soaking, or lubricating solutions can be prepared to provide optimal wearer comfortability. In addition, if cleaning agents are mixed with the ionic 55 polymer solution, mucus, dirt and other unwanted deposits can be removed from the resulting polyelectrolyte complex surface.

Soft and hard synthetic polymer contact lens materials are normally prepared from neutral monomers and/or polymers. In this invention both soft and hard contact lens materials are prepared in such a manner that ionic sites are present on the lens surface, such sites can be reacted with a lens solution containing an 60 oppositely charged, hydrophilic polymer. If the surface of the lens is considered polyanionic, the surface can then be reacted with a hydrophilic polycation with the resulting formation of a hydrophilic polyelectrolyte complex. Polyelectrolyte complexes have an equal amount of cations and anions, each obtained from a different source. In addition, these overall electrically neutral complexes exist as ionically cross-linked hydrogels that are effective in retaining water of hydration. In this invention, a surface coating of 65 polyelectrolyte complex is achieved on a lens surface. A soft contact lens prepared entirely from a

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polyelectrolyte complex is known but would not have the desired properties of lenses preferred in accordance with this invention. In the present invention, it is possible that the reaction of ionic sites on a polymer surface, or potential onic sites, with concommitant release of a low molecular weight electrolyte such as sodium chloride, hydrogen chloride, sodium sulfate, sodium methyl sulfate or any other related selectrolyte could give rise to a monolayer coating of polyelectrolyte complex.

Polyelectrolyte complexes, although highly hydrophilic, are water-insoluble and can be dissolved with some difficulty usually by a ternary solvent system incorporating water, a water-soluble organic compound, and a low molecular weight electrolyte. This solubility behavior implies that in the present invention the polyelectrolyte complex treated surface is very difficult to dissolve and separate from the lens surface by the aqueous fluids of the eve, although this surface coating conceivably could be eroded by mechanical action in the eye during wear. Should dissipation of the polyelectrolyte complex from the lens surface occur, it can readily be replaced by retreatment of the lens with the appropriate oppositely charged polyion solution.

The polyelectrolyte complex on the lens surface can be achieved by several means. If an anionic surface is desired, this can be accomplished by incorporation into the lens formulation of any monomer or monomers from the acrylate or methacrylate salt group, a vinyl suifonate salt, an allyl or methallyl sulfonate or sulfate salt, a styrene sulfonate sait, an acryloyloxy ethyl or methacryloyloxyethyl sulfate salt, a substituted acrylamido, or methacrylamido sulfonate salt or from related phosphonate, phosphate and phosphite salts of polymerizable monomers. Alternatively, a potentially anionic surface can be generated for subsequent treatment with a polycation followed by elimination of a low molecular weight acid (such as hydrogen chloride) or by subsequent treatment with a neutral basic polymer resulting in an acid-base neutralization reaction. Such anionic monomers include compounds such as acrylic and methacrylic acid, vinyl-sulfonic acid, allyl or methallyl sulfonic or sulfuric acid, styrene sulfonic acid, an acrylamido or methacrylamido sulfonic acid, or a polymerisable phosphonic or phosphoric acid.

If a cationic surface is desired, this is accomplished by incorporation into the lens formulation of any quaternary or protonated monomer or monomers from the acrylate or methacrylate salt group, a vinylpyridinium salt, a vinylimidazolium salt, a

vinylimidazole, a vinylbenzyl amine, a vinyl alkyl ether or sulfide, or a polymerizable vinyl phosphine. It is also possible to generate an ionic charge on the lens surface by chemically or electrically modifying a neutral monomeric repeat unit to one that is chargd. For example, an anionic surface can be obtained by treating a polyester material, such as polymethylmethacrylate, with an aqueous base, such as sodium

35 hydroxide, to yield sodium methacrylate units on the lens surface. Alternatively, a polyester material can be hydrolyzed with an acid to yield methacrylic acid units on the lens surface which function as potential anionic sites. Similarly, a cationic surface can be obtained by alkylating or protonating neucleophilic amine, sulfide or phosphine units on the lens surface.

Virtually all hard and soft contact lens materials presently disclosed are electrically neutral polymers or copolymers. Such materials can be modified to include ionic surface groups. One general method for all types of lenses would include treatment of the surface with high energy irradiation in the presence of air to generate ionic surface groups, see A. Chaprio Radiation Chemistry of Polymeric Systems, Vol. XV, Interscience, New York, 1962, and F.A. Makhlis, Radiation Physics and Chemistry of Polymers, Wiley and Sons, New York, 1975.

45 Another method would include modification of polymeric lenses formulations through incorporation of ionic (or potentially ionic) monomers. Polymethyl methacrylate, which is currently the material of choice in the hard lens area, is amenable to such modification. Examples of this approach include the copolymerization of either acrylic acid, methacrylic acid or dimethylaminoethyl methacrylate to provide a polymethyl methacrylate lens with ionic groups on the surface.

Another example would include the modification of oxygen permeable lens formulations such as those in U.S. Patent 3,808,178. These formulations are copolymers of methyl methacrylate with a siloxanylalkyl ester of methacrylic acid and can be modified through the addition of either acrylic acid, methacrylic acid or dimethylaminoethyl methacrylate.

In a similar fashion the monomers acrylic acid, methacrylic acid or dimethylaminoethyl methacrylate
55 could be employed as co-reactants with hydroxyethyl methacrylate to produce a material that is suitable for soft contact lenses which, in addition, provides an ionic surface.

Cellulosic polymers such as cellulose acetate butyrate have found use as contact lenses materials which exhibit moderate oxygen permeability. Polymers of this type contain residual cellulose alcohol functionalities which can be utilized as modification sites. Reaction of sodium chloroacetate with the alcohol functionalities will result in pendent carboxylate groups along the polymer chain. Contact lens produced

60 functionalities will result in pendent carboxylate groups along the polymer chain. Contact lens produced from this modified CAB material would be inherently wettable with an ionic surface receptive to polyelectrolyte complex formation.

The synthetic resin lens preferably has a total ionic charge of from 0.001% to 10%. Thus from 0.001% to 10% of the surface area is charged and the charge density often is about 5%.

65 The lens solutions of this invention are in all cases USP sterile, preferably water solutions containing

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ngred ents common to lens solutions and which carry from 0.001 to 10% by weight of a water soluble ionic polymer or polymers such as:

	polymer or polymers such as:	
	Cationic	5
5	among ymars and copplymers of:	
	the state of the s	
	N,n-dimethylaminoethyladiylate and methylsulfate 2-methacryloyloxyethyltrimethylammonium chloride and methylsulfate	
	2- 4-, and 2-methyl-5-vinylpyridine 2-,4-, and 2-methyl-5-vinylpyridinium chloride and methylsulfate 2-,4-, and 2-methyl-5-vinylpyridinium chloride	1C
	- tdepropy()-N N-dimethyldithic	
10	N-:3-methacrylamidopropyl)-N,N,N-trimethylammonium chloride	
	2	
	1 wind and 2-methyl-1-vinylimidazolium chloride and methyl-1-vinylimidazolium chloride	
		15
15		
13	N in method prior vio Vio VV-2-by droxy in roby in the driving and in	
	dially/dimethylammonium chloride and methyladrate	
	vinylbenzyltrimethylammonium chloride	
	cationic starch	20
20	cationic cellulose	
	ionene polymers	
	Anionic	
	sodium carpoxymethylcellulose	25
	sodium carboxymethylhydroxyethylcellulose	
2	sodium carboxymethylstarch sodium carboxymethylhydroxyethylstarch	
	hydrolyzed polyacrylamide and polyacrylonitrile	
	homopolymers and copolymers of:	
	acrylic and methacrylic acids	30
3	Jan and mothscry/late	
Ī	vinylsulfonic acid	
	sodium vinylfulfonate	
	p-styrenesulfonic acid	35
	sodium p-styrenesulfonate	
3	5 2-methacryloyloxyethylsulfonic acid 3-methacryloyloxy-2-hydroxypropylsulfonic acid	
	3-methacryloyloxy-2-nydroxypropy 2-acrylamido-2-methylpropanesulfonic acid	
	allylsulfonic acid	
	2 chosphatoethyl methacrylate	40
	2-phosphatoethyl methacrylate 2-phosphatoethyl methacrylate 3-phosphatoethyl methacrylate 3-phos	
	and snaking solution additives. Preservatives says as a polyvinyl alcohol,	
	acid (EDTA) mercurials and chilofobutanot can be as a labeling agents such as the wetting	
	bydroxypropyl methylcellulose and methyl cellulose and cleaning agents such as neutral	45
	agents above but in known higher contests and the second on nonvi phenolican be used.	40
	to design the including socium dodecyr surface and the additives are used in a	
	Other conventional buffers, biocides and viscosity modifiers may also be used. The additive did not be of the conventional buffers, biocides and viscosity modifiers may also be used. The additive did not be of the solutions are as near to body pH as wide range of concentrations as known in the art. Preferably the pH of the solutions are as near to body pH as	1
	possible and always in the range of pH 6-8.	
	While it is preterred to merely such the fells in the	50
	while it is preferred to rubbed on the lens surface. 50 sprayed, dropped, or rubbed on the lens surface. In all cases it is preferred to form a coating of no more than 2,500 Å over the lens surface which acts as a lineal cases it is preferred by the polyelectrolyte complex is an ionically cross linked polymer that	
	in all cases it is preferred to form a coating of no more than 2,500 A over the tens survivors linked polymer that	
	In all cases it is preferred to form a coating of no more than 2,500 A over the lens survey of the hydrogel formed by the polyelectrolyte complex is an ionically cross linked polymer that hydrogel. The hydrogel formed by the polyelectrolyte complex is an ionically cross linked polymer that hydrogel. The hydrogel formed by the polyelectrolyte complex is an ionically cross linked polymer that	
	shearne large amounts of water and actions.	55
	absorbs large amounts of water and car be worn for long periods of time. non-irrating to the eye and can be worn for long periods of time.	55
	55 Specific examples of this invention are given bolow 200 and	
	FXAMPLE! set a set all methanizate (MMA) and also from a	
	Hard polymeric test samples were prepared from methyl-methacrylic acid (MA). A minor amount of comonomer mixture of methyl methacrylate (MMA) and methacrylic acid (MA). A minor amount of comonomer mixture of methyl methacrylate (TEGDM) was incorporated in both formulations as a cross-linking agent	
	component mixture of methyl methacrylate (MMA) and methacrylic acid (MA). A film of accomponent mixture of methyl methacrylate (TEGDM) was incorporated in both formulations as a cross-linking agent tetraethyleneglycol dimethacrylate (TEGDM) was incorporated in both formulations as a cross-linking agent tetraethyleneglycol dimethacrylate (TEGDM) was incorporated in both formulations as a cross-linking agent	60
	tetraethyleneglycol dimethacrylate (TEGDM) was incorporated in both formations of tetraethyleneglycol dimethacrylate (TEGDM) was utilized to effect polymerization. The 60 The free radical initiator 2,2'-azobisisobutyronitrile (AIBN) was utilized to effect polymerization. The	
	formulation components (shown in reason as a second in a water path of 40 C and	
	tubes, stoppered, degassed, then allied with integrating a 60°C oven for an additional three days,	
	allowed to polymerize for two days. The tables were then subjected to	
	allowed to polymerize for two days. The tubes were then placed in a 60 constitution of the subjected to after which the polymerized rods were removed from the tubes. The rods were then subjected to after which the polymerized rods were removed from the tubes. The rods were then subjected to after which the polymerization proces conditioning for approximately fifteen hours at 100°C under vacuum to complete the polymerization proces	5 5
	65 conditioning for approximately fifteen flours at 100 0 and 1	

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and relieve any mechanical stresses present. Test specimens, in the form of 3,16" by 1,2" discs, were machined from the conditioned rods. The flat machined surfaces of the discs were then highly polished to provide an appropriate surface for contact angle measurements.

Contact angles were determined on hydrated specimens after immersed in H-O for 2 days with the values 5 representing the advancing water droplet angle on the polished surface. Lower angles are indicative of more wettable materials which can be attributed to a more polar surface either as a result of the chemical groups present or the presence of bound water molecules.

The significantly lower contact angle produced by surface treatment "B" clearly illustrates the embodiment of this invention. The cationic hydroxyethylcellulose is ionically bound to the surface 10 carboxylate (anionic) groups producing a layer of polyelectrolyte complex which contains bound water. TABLE /

15	Composition (wt. percent reagent)				Surface Treatment	Advancing Angle in degrees	15
15	MMA	MA	TEGDM	AZO			13
	98.8	-	1.0	0.2	none	32-84	
	93.8	5	1.0	0.2	none	74-75	
20	93.8	5	1.0	0.2	A*	77-78	20
	93.8	5	1.0	0.2	B**	64 -65	

*Treatment "A" was a five minute immersion in a sodium carbonate water solution (pH = 10.7) followed by a thorough rinse with distilled water.

25 **Treatment "B" was initially identical to treatment "A" with a subsequent five minute immersion in a 0.1 weight percent cationic hydroxyethylcellulose (Union Carbide JR-125 resin) water solution at room temperature followed by a thorough rinse with distilled water. **EXAMPLE II**

Using the experimental procedures described in Example I hard polymeric test samples were prepared 30 from methyl methacrylate (MMA), methacryloyloxypropyl tris(trimethylsilyl) siloxane (TRIS) and methacrylic 30 acid (MA). A minor amount of tetraethylene glycol dimethacrylate (TEGDM) was incorporated as a crosslinking agnt. The free radical initiator 2,2'-azobisisobutyro-nitrile (AIBN) was utilized to effect polymerization. The concentration of reagents employed, surface treatments and contact angle values are presented in Table II, this particular formulation was chosen as typical of those presently utilized in the 35 production of hard, oxygen permeable contact lenses.

TABLE II Composition

40	(wt.	40	
	MMA	59.4	
	TRIS	34.6	
	MA	4.9	
45	TEGDM	0.9	45
	AZO	0.2	
Surface Treatment 50	Advan	cing angle in degrees	50
none	80-82		
"A"	82-83		
"B"	77-78		
"C"*	78-79		
55			55

*Treatment "C" was initially identical to treatment "A" with a subsequent five minute immersion in a 0.1 weight percent polyvinylbenzyl trimethyl ammonium chloride water solution followed by a thorough rinse with distilled water.

EXAMPLE III

Using the experimental procedures described in Example I hard polymeric test samples were prepared from methyl methacrylate (MMA), methacryloyloxypropyl tris(trimethylsilyl) siloxane (TRIS) and dimethylaminoethyl methacrylate (DMAEM). A minor amount of tetraethylene glycol dimethacrylate (TEGDM) was incorporated as a crosslinking agent. The free radical initiator 2,2'-azobisisobutyronitrile (AIBN) was utilized to effect polymerization. The concentration of reagents employed, surface treatments and contact angle 65 values are presented in Table III. This particular composition was chosen as typical of a material which could

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be utilized in the production of highly oxygen permeable, hard contact lenses.

This example illustrates the incorporation of a cationic monomer in the polymer formulation which is receptive to treatment with an anionic polymer to form a surface layer of poly-electrolyte complex. This behavior demonstrates the versatility of the present invention in that either an anionic (Examples I and II) or 5 a cationic (Example III) monomer may be incorporated into a polymeric formulation which is capable of forming a polyelectrolyte complex with a polyion of the opposite charge.

TABLE III

		10	
10	(wt.)	, ,	
10	MMA	51.8	
	TRIS	42.4	
	DMAEM	4.7	
	TEGDM	0.9	15
16	AZO	0.2	Ū
15	Advancing		
Surface Treatment	83-84		
none "D"*	84-85		
'E''**	75-76		20
0 "F"***	77-78		

*Treatment "D" was a five minute immersion in a hydrochloric acid solution (pH = 3.0) followed by a thorough rinse with distilled water.

**Treatment "E" was a five minute immersion in a 0.1 weight percent polyacrylic acid water solution

25 followed by a thorough rinse with distilled water.

***Treatment "F" was initially identical to treatment "D" with a subsequent five minute immersion in a 0.1 weight percent sodium polystyrenesulfonate water solution followed by a thorough rinse with distilled

In general, the polymeric material of the lens is preferably selected from the group comprising:

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the lens is preferably selected from the group comprising.

$$\begin{array}{c}
R_1 \\
CH_2 = C \\
C = O
\end{array}$$
35
$$\begin{array}{c}
C = O \\
C = O
\end{array}$$
36
$$\begin{array}{c}
C = O \\
C = O
\end{array}$$
37
$$\begin{array}{c}
C = O \\
C = O
\end{array}$$
40

40 where $R_1 = H$, CH_3 , CH_2COOH , CH_2COOCH_3 , or $CH_2COOC_6H_5$, and $R_2 = H$, or C_1-C_{20} derivative of a monohydric alkanol, a C₁-C₃ derivative of dihydric and trihydric alkanols, or

$$\begin{array}{c|c}
B \\
A - Si - A
\end{array}$$

$$+CH_2) - Si - O - Si + (O) - D$$

$$A$$

$$A$$

$$\begin{array}{c}
O \\
A - S - A
\end{array}$$

$$\begin{array}{c}
O \\
C \\
C
\end{array}$$

$$\begin{array}{c}
O \\
C
\end{array}$$

$$\begin{array}{c}
O \\
C
\end{array}$$

$$\begin{array}{c}
O \\
C
\end{array}$$

60 where "a" is an integer from one to three, "b" and "c" are integers from zero to two, "d" is an integer from zero to one, A is selected from the class of methyl and phenyl groups, B is selected from the class of methyl

or phenyl groups, C and D represent either no group (cyclic ring from "c" to "d") or methyl or phenyl groups. The polymeric material can also consist essentially of:

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10 where R_1 and R_2 are selected from H, CH_3 , C_2H_5 , C_2H_5 , C_5H_5 , COOH, $CH_2=CH_1$ and -0- groups. 10 In some cases, the polymeric material consists essentially of cellulose units having the formula:

$$\begin{array}{c}
CH_2OR_1\\
-O \longrightarrow O\\
OOO\\
R_2 \longrightarrow R_3
\end{array}$$
15

where R_1 , R_2 and R_3 are selected from H, derivatives of C_1 - C_{20} carboxylic acid, C_1 - C_{20} alkyl groups, C_1 to C_3 monohydric and dihydric alkanols, phenyl groups, CH_2COOH , and $CH_2CH_2\overline{N}R_3$ groups wherein R_4 = H, CH_3 , or C_2H_5 .

While specific polymers described can be used alone, they can also be used in combination with each other. For example, the lens composition can comprise a mixture of two or more different derivatives of acrylic or methacrylic acid. It is important that the ionic charge be present and that the polymer or polymer mixture provide good contact lens characteristics as known in the art such as optical clarity.

Preferably the contact lenses have a lens surface which contain ionic sites which are complexed to oppositely charged polymer sites selected from the groups COOX, SO_3X , and PO_3X , wherein X=H or monovalent inorganic ion \bar{N} (R)₃ groups, wherein R=H, CH_3 or C_2H_5 groups, $\bar{S}(R')_2$, wherein R'=H, CH_3 , or C_2H_5 groups, $\bar{P}(R'')_3$, wherein R''=H, CH_3 , C_2H_5 and phenyl groups, pridinium groups and imidazolium groups.

35 What is claimed is: 35

CLAIMS

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1. A contact lens comprising an optically clear, transparent body having a lens surface, said lens surface defining a polymeric material carrying an ionic charge, a thin layer of a polyelectrolyte complex coating said lens surface and electrostatically bound thereto, said coating comprising an ionic polymer and said polymer forming a hydrogel at the surface which absorbs water, has good water retention and is compatible with the physiological structure of the eye.

A contact lens in accordance with claim 1 wherein said polymeric material is:

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$$\begin{array}{c}
R_{1} \\
CH_{2} = C \\
C \cdot O \\
C \cdot O \\
R_{2}
\end{array}$$
50

where $R_1 = H$, CH_3 , CH_2COOH , CH_2COOCH_3 , or $CH_2COOC_6H_5$, and $R_2 = H$, or C_1-C_{20} derivative of a monohydric alkanol, a C_1-C_3 derivative of dihydric and trihydric alkanols, or

where "a" is an integer from one to three, "b" and "c" are integers from zero to two, "d" is an integer from zero to one, A is selected from the class of methyl and phenyl groups, B is selected from the class of methyl 20 or pnenyl groups, C and D represent either no group (cyclic ring from "c" to "d") or methyl or phenyl groups.

3. A contact lens in accordance with claim 1 and further comprising said polymeric material consisting essentially of

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where R_1 and R_2 are selected from H, CH₃, C_2H_5 , C_3H_7 , C_6H_5 , COOH, CH₂=CH- and -0- groups.

4. A contact iens in accordance with claim 1 and further comprising said polymeric material consisting assentially of cellulose units having the formula

where R_1 , R_2 and R_3 are selected from H, derivatives of C_1 - C_{20} carboxylic acid, C_1 - C_{20} alkyl groups, C_1 to C_3 monohydric and dihydric alkanols, phenyl groups, CH_2COOH , and $CH_2CH_2\tilde{N}$ R_3 groups, wherein $R_4 = H$, CH_3 , or C_2H_5 .

- 50 5. A contact lens in accordance with claim 1 wherein said lens surface contains ionic sites which are complexed to oppositely charged polymer sites selected from the groups COOX, SO₃X, and PO₃X, wherein X = H or monovalent inorganic ion, N(R)₃ groups, wherein R = H, CH₃ or C₂H₅ groups, Š(R')₂, wherein R' = H, CH₃, or C₂H₅ groups, P(R'')₃, wherein R'' = H, CH₃, C₂H₅ and phenyl groups, pyridinium groups and imidazolium groups.
- 55 6. A contact lens in accordance with claim 1 wherein said lens surface has a total ionic charge of from 0.001% to 10%.
 - 7. A contact lens in accordance with claim 6 wherein said thin layer of polyelectrolyte complex coating has a thickness in the range of from 20 to 2,500 Angstroms.
- 8. A contact lens in accordance with claim 2 wherein said lens surface contains ionic sites which are 60 complexed to oppositely charged polymer sites selected from the groups COOX, SO₃X, and PO₃X, wherein X = H or monovalent inorganic ion, $\tilde{N}(R')_3$ groups, wherein R = H, CH₃ or C₂H₅ groups, \tilde{S} (R')₂, wherein R' = H, CH₃, or C₂H₅ groups, $\tilde{P}(R'')_3$, wherein R'' = H, CH₃, C₂H₅ and phenyl groups, pyridinium groups and imidazolium groups.
- 9. A contact lens in accordance with claim 3 wherein said lens surface contains ionic sites which are 65 complexed to oppositely charged polymer sites selected from the groups COOX, SO₃X, and PO₃X, wherein X 65

described and exemflified.

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= H or monovalent inorganic ion, $\tilde{N}(R)_3$ groups, wherein $R=H$, CH_3 or C_2H_5 groups, $\tilde{S}(R')_2$ wherein $R'=H$, CH_3 , or C_2H_5 groups, $\tilde{P}(R'')_3$, wherein $R'=H$, CH_3 , C_2H_5 and phenyl groups, pyridinium groups and imidazolium groups.	
10. A contact lens in accordance with claim 4 wherein said lens surface contains ionic sites which are 5 complexed to oppositely charged polymer sites selected from the groups COOX, SO_3X , and PO_3X , wherein $X = H$ or monovalent inorganic ion, $\tilde{N}(R)_3$ groups, wherein $R = H$, CH_3 or C_2H_5 groups, $\tilde{S}(R')_2$, wherein $R' = H$, CH_3 , or C_2H_5 groups, $\tilde{S}(R')_3$, wherein $R' = H$, CH_3 , C_2H_5 and phenyl groups, pyridinium groups and	5
imidazolium groups.	
11. A contact lens in accordance with claim 7 wherein said lens surface contains ionic sites which are 10 complexed to oppositely charged polymer sites selected from the groups COOX, SO ₃ X, and PO ₃ X, wherein X = H or monovalent inorganic ion, $\tilde{N}(R)_3$ groups, wherein $R = H$, CH_3 or C_2H_5 groups, $\tilde{S}(R')_2$, wherein $R' = H$,	10
CH ₃ , or C_2H_5 groups, $\tilde{P}(R^n)_3$, wherein $R^n=H$, CH ₃ , C_2H_5 and phenyl groups, pyridinium groups and	
imidazolium groups.	
12. A lens solution for treating contact lens surfaces, said lens solution consisting essentially of an ionic	
15 polymer in water solution with said polymer being present in an amount of from 0.001 to 10% by weight of	15
said solution,	
said solution being sterile and having a physiologically acceptable pH.	
13. A lens solution in accordance with the lens solution of claim 12 and further comprising lens cleaning	
and preserving additives.	20
20 14. A method of forming a polyelectrolyte complex coating on a polymeric lens, said method	20
comprising,	
wetting said lens surface with a wetting solution carrying an ionic polymer to form a thin layer of said	
polylectrolyte complex electrostatically bound to said surface,	
said coating comprising an ionic polymer and said polymer forming a hydrogel at said surface which	25
25 absorbs water, has good water retention and is compatible with the physiological structure of the eyes.	
15. Contact lenses according to claim 1,esubstantially as hereinbefore decribed and exemplified.	
16. A solution for treating contact lens surfaces, substantially as hereinbefore described and examflified.	
17. A method according to claim 14 of forming a coating on a contact lens, substantially as hereinbefore	

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AN - 89-223299 ¢31!

AP - JP860308716 861226

PR - JP8-0308716 361226

- Washing and preserving soln, for contact lens contains water-soluble cationic polymer dissolved in saline soln. or pure water

IW - WASHING PRESERVE SOLUTION CONTACT LENS CONTAIN WATER SOLUBLE CATION POLYMER DISSOLVE SALINE SOLUTION PURE WATER

- (DAIL) DAIGEL CHEM IND LTD PA

PN - JP1158412 A 890621 DW8931 003pp

ORD - 1989-06-21

IC - C11D17/00 ; G02C7/04 ; G02C13/00

FS - CPI; GMPI

DC - A18 A96 D22 P81

AB - J01158412 Soln. contains water-soluble cationic polymer, which is dissolved in physiological saline solm, or pure water.

- The cationic polymer of natural polysaccharide such as cellulose, starch, tamarind, etc. and their derivs. to which are added alkylene oxide or glycidol is used. Cationic polyvinyl pyrrolidone, cationic polyacrylic acid, etc. and their derivs. can be used. The mixts. of at least two kinds of cationic polymers can be used. The amt. of the cationic polymer to soln. is 0.01-5 wt.%, pref. 0.01-2 wt.%. The buffer agent and other additives can be used.

- USE/ADVANTAGE - Used for washing and preserving soln. for contact lens. The soln. has both functions for washing and preservation. It keeps hydrophilic property of the lens surface and suppresses the reproduction of bacteria. The addn. of germicide is not needed. (0/0)